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# Hydrothermal synthesis and crystal structures of new uranyl oxalate hydroxides: α- and β-$[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ and $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2] \cdot H_2O$

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## Abstract

Two modifications of the new uranyl oxalate hydroxide dihydrate $[UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ (**1** and **2**) and one form of the new uranyl oxalate hydroxide trihydrate $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2] \cdot H_2O$ (**3**) were synthesized by hydrothermal methods and their structures determined from single-crystal X-ray diffraction data. The crystal structures were refined by full-matrix least-squares methods to agreement indices $R(wR) = 0.0372(0.0842)$ and $0.0267(0.0671)$ calculated for 1096 and 1167 unique observed reflections ($I > 2\sigma(I)$), for α (**1**) and β (**2**) forms, respectively and to $R(wR) = 0.0301(0.0737)$ calculated for 2471 unique observed reflections ($I > 2\sigma(I)$), for **3**. The α-form of the dihydrate is triclinic, space group $P\bar{1}$, $Z = 1$, $a = 6.097(2)$, $b = 5.548(2)$, $c = 7.806(3)$ Å, $\alpha = 89.353(5)$, $\beta = 94.387(5)$, $\gamma = 97.646(5)°$, $V = 260.88(15)$ Å$^3$, β-form is monoclinic, space group $C2/c$, $Z = 4$, $a = 12.180(3)$, $b = 8.223(2)$, $c = 10.777(3)$ Å, $\beta = 95.817(4)$, $V = 1073.8(5)$ Å$^3$. The trihydrate is monoclinic, space group $P2_1/c$, $Z = 4$, $a = 5.5095(12)$, $b = 15.195(3)$, $c = 13.398(3)$ Å, $\beta = 93.927(3)$, $V = 1119.0(4)$ Å$^3$. In the three structures, the coordination of uranium atom is a pentagonal bipyramid composed of dioxo $UO_2^{2+}$ cation perpendicular to five equatorial oxygen atoms belonging to one bidentate oxalate ion, one water molecule and two hydroxyl ions in *trans* configuration in **2** and in *cis* configuration in **1** and **3**. The $UO_7$ polyhedra are linked through hydroxyl oxygen atoms to form different structural building units, dimers $[U_2O_{10}]$ obtained by edge-sharing in **1**, chains $[UO_6]_\infty$ and tetramers $[U_4O_{26}]$ built by corner-sharing in **2** and **3**, respectively. These units are further connected by oxalate entities that act as bis-bidentate to form one-dimensional chains in **1** and bi-dimensional network in **2** and **3**. These chains or layers are connected in frameworks by hydrogen-bond arrays.

*Keywords:* Uranyl oxalate; Hydrothermal synthesis; Crystal structure refinement

## 1. Introduction

The renewal of interest in the last decades in the crystal chemistry of compounds containing uranyl ion associated with inorganic oxo-anion such as molybdate [1–9], tungstate [10–13], vanadate [14–21], etc. reflects their considerable compositional range, chemical and structural diversity with various dimensionality, properties and potential applications in nuclear industry, ion-exchange or catalysis and high environmental relevance.

On the other hand, complexes of uranyl ion with the simplest organic ligand containing carbonyl-group, the oxalate ion, have also attracted a great deal of interest because of their great versatility, the important role of the oxalic acid as precipitating agent in the nuclear fuel technology or for waste decontamination purpose or as complexing agent to adjust extracting characteristics of actinides and lanthanides or redox behavior of actinides. They can also contribute to model the migration of the radionuclides in the environment because the most important mechanism is the complexation of radionuclides by carboxylic functional groups of natural humic acids from water [22].

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Our group has recently focused on the synthesis and crystal structure study of oxalate complexes containing U(VI) [23] or U(IV) and sometimes Ln(III) [24,25].

A lot of work, devoted to the combination of uranyl cation $UO_2^{2+}$ and oxalate ligand $C_2O_4^{2-}$, in the presence of monovalent cation $M^+$ ($M^+ = Na^+$, $K^+$, $N_2H_5^+$ or $NH_4^+$), have investigated various $UO_2^{2+}/C_2O_4^{2-}$ ratios and permitted to solve some original structures [26–36]. The oxalate ions can act as monodentate, bidentate, tridentate or tetradentate chelating ligand and lead to the formation of several types of arrangements: (1) isolated anions $[UO_2(C_2O_4)_2H_2O]^{2-}$ with five coordinated uranyl ion in $(N_2H_5)_2[UO_2(C_2O_4)_2H_2O]$ [36], $(NH_4)_2[UO_2(C_2O_4)_2H_2O]\cdot 2H_2O$ [23] and $Na_2[UO_2(C_2O_4)_2H_2O]\cdot 4H_2O$ [26] or $[UO_2(C_2O_4)_3]^{4-}$ for six coordinated uranyl ion in $(NH_4)_4UO_2(C_2O_4)_3$ [26], in which oxalate ions are non-bridging, (2) dimeric isolated anions containing two uranium atoms when two bidentate oxalate anion are non-bridging and one links the two $(UO_2)^{2+}$ ions, in $M_6[(UO_2)_2(C_2O_4)_5]\cdot xH_2O$ ($M = K$ [34], $N_2H_5$ [35]), (3) $[UO_2(C_2O_4)_2]_\infty$ chains in $(NH_4)_2[UO_2(C_2O_4)_2]$ [29], (4) double chains in $(NH_4)_2[(UO_2)_2(C_2O_4)_3]$ [30], (5) six-membered rings arranged in honeycomb layers as in $K_2[(UO_2)_2(C_2O_4)_3]\cdot 4H_2O$ [31], $(NH_4)_2[(UO_2)_2(C_2O_4)_3]\cdot 3H_2O$ and $(NH_4)(N_2H_5)[(UO_2)_2(C_2O_4)_3]\cdot 3H_2O$ [23] or ten-membered rings arranged in layers in $Na_2[(UO_2)_4(C_2O_4)_5(H_2O)_2]\cdot 8H_2O$ [27]. The presence of uranyl bonds perpendicular to the layers prevents the linkage in the third dimension, thus no three-dimensional arrangement of uranyl ions and oxalates entities has been reported. In $[UO_2(C_2O_4)]\cdot 3H_2O$ [32,33], the only uranyl oxalate free of monovalent countercation known up to date, $[UO_2(C_2O_4)H_2O]_\infty$ chains where $UO_2^{2+}$ alternate with tetradentate $(C_2O_4)^{2-}$ anions are linked together by water molecules through hydrogen bonds. Finally, two uranyl oxalato-hydroxides have been reported, $NH_4[(UO_2)_2(C_2O_4)_2(OH)_2]\cdot 2H_2O$ [37] which contains similar chains, and $Na_4(UO_2)_2(C_2O_4)_2(OH)_4]$ [38,39] with unknown structure.

When available, single crystals of the compounds were all prepared from slow evaporation from solutions. In the present study we report the synthesis of two forms of a new uranyl oxalate hydroxide dihydrate obtained by hydrothermal synthesis allowing the absence of monovalent countercation. Astonishingly, using a starting mixture containing $K^+$ led to the formation of the corresponding uranyl oxalate hydroxide trihydrate. The crystal structure of the three uranyl oxalate hydroxides is reported.

## 2. Experimental

### 2.1. Synthesis

Yellow prismatic crystals of $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ were prepared under mild hydrothermal conditions from mixtures of uranium oxide $U_3O_8$ (1 mmol), oxalic acid (2 mmol) and water (6 mL). Reactions were run in Teflon-lined stainless-steel 23-mL autoclaves. The resulting products were filtered after cooling, washed with distilled water and dried at room temperature. X-ray examination showed the existence of two forms of $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ ($\alpha$ and $\beta$) depending on the synthesis conditions. $\alpha$-Type crystals (**1**) among a small quantity of $U_3O_8$ powder were obtained after two weeks heating at 190 °C (autogeneous pressure). $\beta$-Type crystals (**2**), accompanied with $UO_2(C_2O_4)\cdot 3H_2O$ crystals among $U_3O_8$ powder, were grown after a one week heating at 150 °C (autogeneous pressure). Yellow single crystals of the trihydrate $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]\cdot H_2O$ (**3**) were obtained starting from a mixture of uranium nitrate $(UO_2)(NO_3)_2\cdot 6H_2O$ (0.502 g, 1 mmol), potassium nitrate $KNO_3$ (0.1011 g, 1 mmol), oxalic acid (0.2521 g, 2 mmol) and water (6 mL), maintained four days at 120 °C in the same autoclave. Note that the use of $NaNO_3$ (0.0850 g, 1 mmol) instead of $KNO_3$ led to the growth of single crystals of $[UO_2(C_2O_4)]\cdot 3H_2O$ in these synthesis conditions [32].

### 2.2. Single-crystal data collection

Suitable crystals of the three compounds were selected under an optical microscope for the X-ray diffraction study and were mounted on a Bruker SMART CCD 1K diffractometer. The intensities for the whole reciprocal space were measured using graphite monochromated Mo$K\alpha$ radiation and extracted from the collected frames using the program SaintPlus 6.02 [40]. Structure calculations were performed with the SHELXTL package [41]. Unit cell parameters were refined and an empirical absorption correction was applied using the program SADABS of the SHELXTL package [42]. Selected data collection parameters and crystallographic characteristics are provided in Table 1. Additional details can be found in Supporting Information.

## 3. Structure solution and refinement

For the three crystal structure determinations, the uranium atoms were located using the Patterson function, while the remaining atoms (C and O) were found from successive Fourier map analyses. The location of the H atoms was not determined because of the presence of the very heavy U atoms and important thermal agitation of water molecules. The atomic positions for all non-H atoms and the anisotropic displacement parameters were included in the last cycles of refinement.

The structure of **1** was determined and refined in the centrosymmetric triclinic space group $P\bar{1}$. Final atomic parameters are given in Table 2. The structure, refined on $F^2$, converged for 1096 unique reflections and 73 parameters to give $R = 0.0372$ and w$R = 0.0842$.

The structure of **2** was solved in space group $C2/c$. A structure model including all non-H atoms converged to reliability factors $R = 0.0267$, w$R = 0.0671$ with 1167

Table 1
Crystal data and structure refinement for α-$[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ (**1**), β-$[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ (**2**) and $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]\cdot H_2O$ (**3**)

| | Compound **1** | Compound **2** | Compound **3** |
|---|---|---|---|
| Empirical formula | $U_2C_2O_{12}H_6$ | $U_2C_2O_{12}H_6$ | $U_2C_2O_{13}H_8$ |
| Formula weight | 698.13 | 698.13 | 716.14 |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | *P*-1 | *C*2/*c* | *P*21/*c* |
| *a* (Å) | 6.097(2) | 12.180(3) | 5.5095(12) |
| *b* (Å) | 5.547(2) | 8.223(2) | 15.195(3) |
| *c* (Å) | 7.806(3) | 10.777(3) | 13.398(3) |
| α (deg) | 89.353(5) | 90 | 90 |
| β (deg) | 94.387(5) | 95.817(4) | 93.927(3) |
| γ (deg) | 97.646(5) | 90 | 90 |
| Volume ($Å^3$) | 260.8(2) | 1073.8(5) | 1119.0(4) |
| *Z* | 1 | 4 | 4 |
| Density calculated | 4.444 | 4.318 | 4.251 |
| Absorption coefficient ($mm^{-1}$) | 31.055 | 30.180 | 28.972 |
| *F* (000) | 298 | 1192 | 1232 |
| Temperature (K) | 293(2) | 293(2) | 293(2) |
| Theta range for data collection | 2.62–27.82° | 2.99–27.95° | 2.03–27.98° |
| Index ranges | $-7\leqslant h\leqslant 7$, $-7\leqslant k\leqslant 7$, $-10\leqslant l\leqslant 9$ | $-15\leqslant h\leqslant 15$, $-10\leqslant k\leqslant 10$, $-13\leqslant l\leqslant 14$ | $-6\leqslant h\leqslant 6$, $-19\leqslant k\leqslant 19$, $-16\leqslant l\leqslant 17$ |
| Reflections collected | 2038 | 3872 | 8629 |
| Independent reflections | 1096 [*R*(int) = 0.0418] | 1167 [*R*(int) = 0.0363] | 2471 [*R*(int) = 0.0406] |
| Completeness to $\theta = 27.82°$ | 88.7% | 90.5% | 91.7% |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/resraints/parameters | 1096/0/73 | 1167/0/73 | 2471/0/155 |
| Goodness-of-fit on $F_2$ | 0.999 | 1.076 | 1.047 |
| Final *R* indices [$I>2\sigma(I)$], $R_1$/w$R_2$ | 0.0372, 0.0842 | 0.0267, 0.0671 | 0.0301, 0.0737 |
| *R* indices (all data), $R_1$/w$R_2$ | 0.0410, 0.0862 | 0.0324, 0.0689 | 0.0342, 0.0757 |
| Largest diff. peak/hole | 2.642/−3.107 e $Å^{-3}$ | 2.413/−2.195 e $Å^{-3}$ | 2.539 and −2.373 e $Å^{-3}$ |

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for the α-form of $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ (**1**)

| Atom | Site | *x* | *y* | *z* | $U_{(eq)}$ |
|---|---|---|---|---|---|
| U(1) | 2*i* | 0.85247(7) | 0.13427(7) | 0.29675(5) | 0.014(1) |
| C(1) | 2*i* | 0.883(2) | 0.4731(19) | −0.0469(13) | 0.018(2) |
| O(1) | 2*i* | 0.9207(14) | −0.1068(15) | 0.1746(10) | 0.021(2) |
| O(2) | 2*i* | 0.7716(14) | 0.3691(15) | 0.4187(10) | 0.019(2) |
| O(3) | 2*i* | 0.7455(13) | 0.3234(15) | 0.0225(10) | 0.018(2) |
| O(4) | 2*i* | 1.1450(13) | 0.4180(15) | 0.1845(10) | 0.021(2) |
| O(5) | 2*i* | 0.8053(14) | −0.1278(14) | 0.535(1) | 0.021(2) |
| O(6) | 2*i* | 0.4712(14) | −0.0266(16) | 0.2454(11) | 0.025(2) |

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

reflections and 73 parameters. The final atomic coordinates are reported in Table 3.

Finally, the studied crystal of **3** presented systematic extinction conditions consistent with centrosymmetric *P*21/*c* space group. The refinement of the atomic coordinates and of the anisotropic displacement parameters for all non-H atoms led to the reliability factors $R = 0.0301$, w$R = 0.0737$ with 2471 reflections and 155 parameters and the final atomic parameters listed in Table 4.

## 4. Results and discussion

Selected distances and angles are reported in Table 5 for **1** and **2** and in Table 6 for **3**.

The three structures are built from $UO_7$ pentagonal bipyramids sharing hydroxyl oxygen atoms to form polymeric entities, called hereafter the structural polyhedral building units SPBU, further connected through oxalate ions to create neutral one (1D) or two (2D) dimensional networks.

### 4.1. Uranium polyhedron

In each of the structure presented in this study the U(VI) cations are bonded to two oxygen atoms at short distances, forming nearly linear $(O{=}U{=}O)^{2+}$ uranyl ions with U=O bond lengths in the narrow range 1.758(6)–1.775(6) Å, slightly lower than the average value of 1.79(4) Å calculated by Burns et al. [43] from 93

Table 3
Atomic coordinates and equivalent isotropic displacement parameters for the $\beta$-form of $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ (**2**)

| Atom | Site | $x$ | $y$ | $z$ | $U_{(eq)}$ |
|---|---|---|---|---|---|
| U(1) | $8f$ | 0.28913(2) | 0.02761(3) | 0.79640(3) | 0.019(1) |
| C(1) | $8f$ | 0.4888(12) | 0.0890(18) | 1.0220(14) | 0.021(2) |
| O(1) | $8f$ | 0.3720(4) | 0.1049(7) | 0.6850(5) | 0.026(1) |
| O(2) | $8f$ | 0.2063(5) | −0.0453(7) | 0.9088(5) | 0.028(1) |
| O(3) | $8f$ | 0.4065(4) | 0.1590(6) | 0.9708(5) | 0.026(1) |
| O(4) | $8f$ | 0.4431(4) | −0.1418(6) | 0.8915(5) | 0.026(1) |
| O(5) | $8f$ | 0.2165(4) | 0.2845(6) | 0.8163(5) | 0.022(1) |
| O(6) | $8f$ | 0.1203(5) | 0.0369(6) | 0.6446(7) | 0.033(2) |

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 4
Atomic coordinates and equivalent isotropic displacement parameters for $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]\cdot H_2O$ (**3**)

| Atom | Site | $x$ | $y$ | $z$ | $U_{(eq)}$ |
|---|---|---|---|---|---|
| U(1) | $4e$ | 0.22247(5) | 0.45998(2) | 0.28611(2) | 0.011(1) |
| U(2) | $4e$ | −0.47319(5) | 0.18519(2) | 0.04274(2) | 0.009(1) |
| C(1) | $4e$ | −0.1310(13) | 0.3524(5) | 0.1186(5) | 0.010(1) |
| C(2) | $4e$ | −0.1076(14) | 0.2884(5) | 0.2079(6) | 0.013(2) |
| O(11) | $4e$ | 0.4791(10) | 0.4069(4) | 0.2417(4) | 0.018(1) |
| O(12) | $4e$ | −0.0365(10) | 0.5153(4) | 0.3270(4) | 0.013(1) |
| O(13) | $4e$ | 0.0251(10) | 0.3133(3) | 0.2820(4) | 0.012(1) |
| O(14) | $4e$ | −0.0143(10) | 0.4229(3) | 0.1293(4) | 0.013(1) |
| O(5) | $4e$ | 0.4842(9) | 0.5614(3) | 0.3581(4) | 0.012(1) |
| O(5′) | $4e$ | −0.7402(9) | 0.1031(4) | −0.0566(4) | 0.012(1) |
| O(16) | $4e$ | 0.2217(11) | 0.5827(4) | 0.1645(4) | 0.021(1) |
| O(21) | $4e$ | −0.7209(10) | 0.2299(4) | 0.1027(4) | 0.014(1) |
| O(22) | $4e$ | −0.2242(10) | 0.1398(4) | −0.0170(4) | 0.012(1) |
| O(23) | $4e$ | −0.2198(9) | 0.2166(3) | 0.1982(4) | 0.011(1) |
| O(24) | $4e$ | −0.2618(10) | 0.3288(4) | 0.0446(4) | 0.014(1) |
| O(26) | $4e$ | −0.6107(10) | 0.2782(4) | −0.1022(4) | 0.017(1) |
| O(7) | $4e$ | −0.3236(19) | 0.5547(4) | 0.0486(5) | 0.051(3) |

$U_{(eq)}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 5
Significant bond lengths [Å] and angles [deg] with bond valence for U–O and C–O bonds in $(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2$ (**1**) and (**2**)

| Compound | **1** | Valence bond | **2** | Valence bond |
|---|---|---|---|---|
| U(1)–O(1) | 1.763(7) | 1.74 | 1.763(6) | 1.74 |
| U(1)–O(2) | 1.766(7) | 1.73 | 1.758(6) | 1.75 |
| U(1)–O(5) | 2.359(8) | 0.54 | 2.308(5) | 0.60 |
| U(1)–O(5)#1 | 2.383(9) | 0.51 | 2.336(5) | 0.56 |
| U(1)–O(6) | 2.382(8) | 0.52 | 2.495(5) | 0.41 |
| U(1)–O(3) | 2.455(8) | 0.45 | 2.489(5) | 0.42 |
| U(1)–O(4) | 2.426(8) | 0.47 | 2.474(5) | 0.43 |
| O(1)–U(1)–O(2) | 177.4(4) |  | 178.8(2) |  |
| C(1)–O(3) | 1.248(13) | 1.47 | 1.244(8) | 1.48 |
| C(1)–O(4) | 1.238(14) | 1.51 | 1.257(8) | 1.43 |
| C(1)–C(1) | 1.55(2) |  | 1.560(15) |  |

Symmetry transformations used to generate equivalent atoms: #1 2−x, −y, 1−z for (**1**) and 1/2−$x$, $y$−1/2, 3/2−$z$ for (**2**).

compounds containing $UO_7$ polyhedra. Each uranyl ion is coordinated in the equatorial plane by five oxygen atoms, two hydroxyl oxygen atoms, one belonging to a water molecule, and two that pertain to one oxalate ions which act as bidentate, to give a pentagonal bipyramidal environment (Fig. 1a and b). However, the relative positions of the various hydroxyl and water oxygen atoms together with their distances to U are different for the three

Table 6
Significant bond lengths [Å] and angles [deg] with bond valence for U–O and C–O bonds in $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]\cdot H_2O$ (**3**)

| U(1) | | Valence bond | U(2) | | Valence bond |
|---|---|---|---|---|---|
| U(1)–O(11) | 1.766(6) | 1.73 | U(2)–O(21) | 1.767(5) | 1.72 |
| U(1)–O(12) | 1.775(6) | 1.70 | U(2)–O(22) | 1.774(5) | 1.70 |
| U(1)–O(5) | 2.279(5) | 0.63 | U(2)–O(5) | 2.306(5) | 0.60 |
| U(1)–O(5′) | 2.311(5) | 0.59 | U(2)–O(5′) | 2.286(5) | 0.62 |
| U(1)–O(13) | 2.479(5) | 0.43 | U(2)–O(23) | 2.473(5) | 0.43 |
| U(1)–O(14) | 2.461(5) | 0.44 | U(2)–O(24) | 2.473(5) | 0.43 |
| U(1)–O(16) | 2.476(6) | 0.43 | U(2)–O(26) | 2.478(5) | 0.43 |
| O(11)–U(1)–O(12) | 178.1(3) | | O(21)–U(2)–O(22) | 179.7(3) | |
| C(2)–O(13) | 1.250(9) | 1.46 | | | |
| C(1)–O(14) | 1.252(9) | 1.45 | | | |
| C(2)–O(23) | 1.256(9) | 1.44 | | | |
| C(1)–O(24) | 1.239(9) | 1.50 | | | |
| C(1)–C(2) | 1.541(11) | | | | |

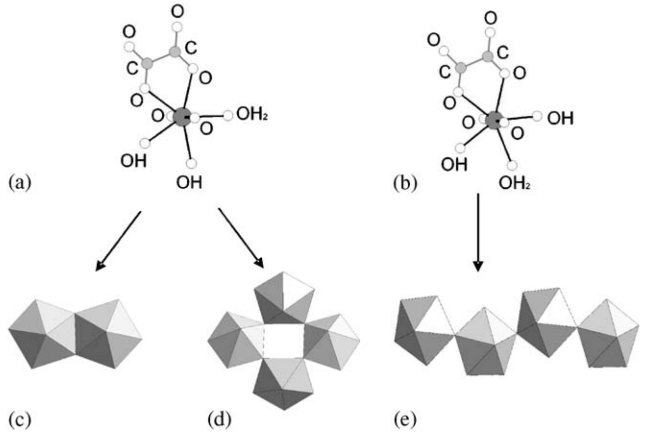

Fig. 1. The two configurations of the $(UO_2)_2O_2(OH)_2(H_2O)$ pentagonal bipyramids with hydroxyl groups in *cis* positions in the α-form of $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ (**1**) and in $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]\cdot H_2O$ (**3**) (a) and in *trans* positions in the β-form of $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ (**1**) (b), and the structural building units, (c) dimer of two edge-shared polyhedra in **1**, (d) tetramer of four corner-shared polyhedra in **3** and (e) linear chain of *trans* corner-shared polyhedra in **2**.

compounds. Whereas in **2** the two hydroxyl oxygens are in *trans* positions (Fig. 1b), in **1** and **3** they are in *cis* positions (Fig. 1a) with slightly shorter average $U–O_{eq}$ distances: 2.420(4) Å in **2**, 2.401(3) Å in **1** and 2.401(3) and 2.403(3) Å for U(1) and U(2) in **3**, respectively. Furthermore, in **1**, the $U–O(H_2O)$ distance is comparable to the U–O(OH) distances whereas in **2** and **3** it is significantly longer and comparable to the U–O(Oxalate) distances.

The coordination and the valence bond sum, calculated using the parameters for U(VI) in seven coordination ($R_{ij} = 2.045$ Å, $b = 0.51$ Å) taken from Burns et al. [43], for the one independent uranium atom in **1** (5.96 vu) and **2** (5.91 vu) and for the two symmetrically independent uranium in **3** (5.95 vu for both U(1) and U(2)) are in agreement with the presence of U(VI) in pentagonal bipyramid polyhedra.

## *4.2. Connectivity of the structures*

The structure of 1 consists of 1D chains $[UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ made up of $UO_7$ units which share edges through hydroxyl oxygen atoms, forming dimeric components $[U_2O_{10}]$ which are the SPBU (Fig. 1c), further connected by bridging oxalate ligands (Fig. 2). The intra-dimer U–U distance of 3.906(1) Å is comparable to those obtained in compounds containing such dimeric cluster of OH–OH bridged uranium pentagonal bipyramids that occurs as isolated in $[UO_2(OH)Cl(H_2O)_2)]$ [44] and in the mineral vandenbrandeite $Cu(UO_2)_2(OH)_4$ [45] with U–U distances of 3.944(5) and 3.887(12) Å, respectively. There is no other constituent between the chains, so the adjacent chains are linked by hydrogen bonds only. As is usually the case for heavy atoms-containing phases such as uranium phases, the data does not allow the resolution of the H atoms, however a network of hydrogen bonds can be imagined involving the shortest O–O distances of 2.921(11) Å (O(5)···O(2)), 2.715(13) Å (O(6)···O(5)) and 2.812(11) Å (O(6)···O(3)). Thus a $[U_2O_{10}]$ dimer of one chain is connected to six other chains where O(5) is donor for the O(5)···O(2) hydrogen bond and O(6) is donor for two O(6)···O(5) and O(6)···O(3) hydrogen bonds with a O(5)–O(6)–O(3) angle of 114.2(4)°.

In **2** polymerization of the uranyl polyhedra occurs by sharing the *trans* OH equatorial vertices, resulting in chains running down the [010] direction which constitute the SPBU (Fig. 1e). The U–U distance is obviously higher than in the dimeric SPBU, 4.3152(12) Å. Adjacent chains are linked by oxalate ions to form a bidimensional network of six-membered rings parallel to the $(\bar{1}01)$ plane (Fig. 3). Adjacent layers are linked by hydrogen bonds that extend between adjacent SPBU from the O(6) and O(5) atoms to O(2) and O(3) atoms of adjacent chains with distances of 2.813(20) and 2.888(14) Å, respectively. Note that O(6) acts also as donor for an intra SPBU hydrogen bond to O(4) atom (O(6)···O(4) = 2.775(15) Å).

In **3** each pentagonal bipyramid share its OH vertices with two other $UO_7$ bipyramids to form tetrameric SPBU

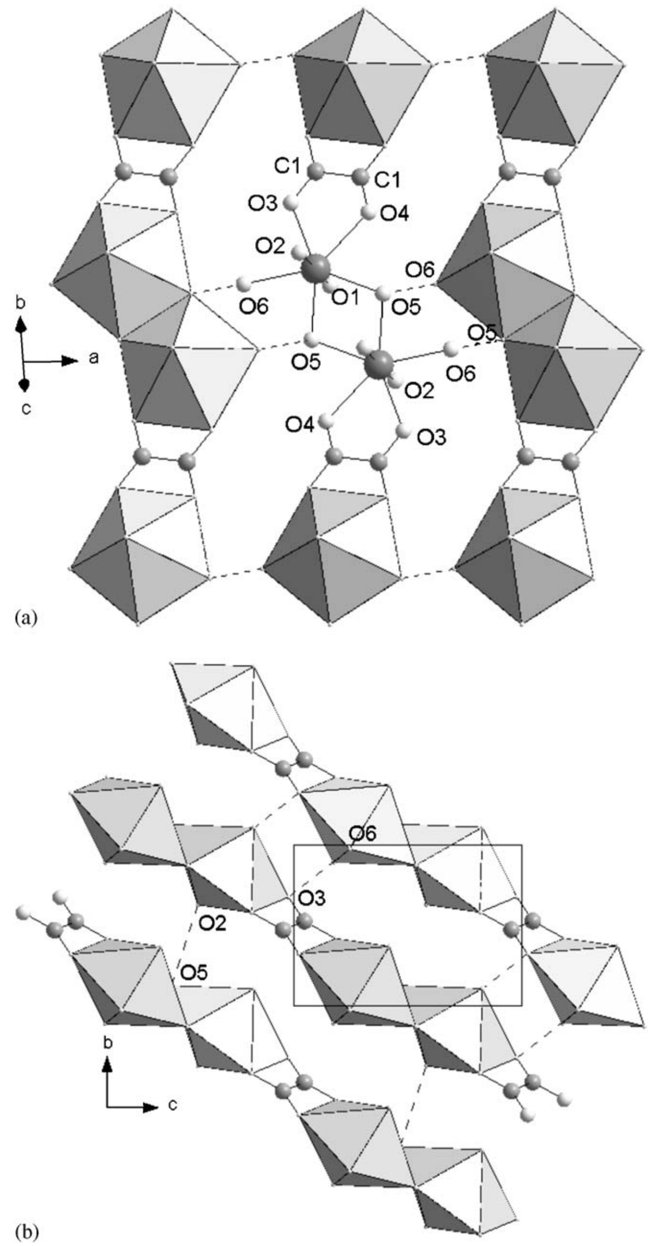

Fig. 2. Projection of the structure of **1** on (a) the (011) plane and (b) the (100) plane showing the connection of the SPBU of two edge-shared pentagonal bipyramids through oxalate entities to form one-dimensional chains linked together by a three-dimensional network of hydrogen bonds.

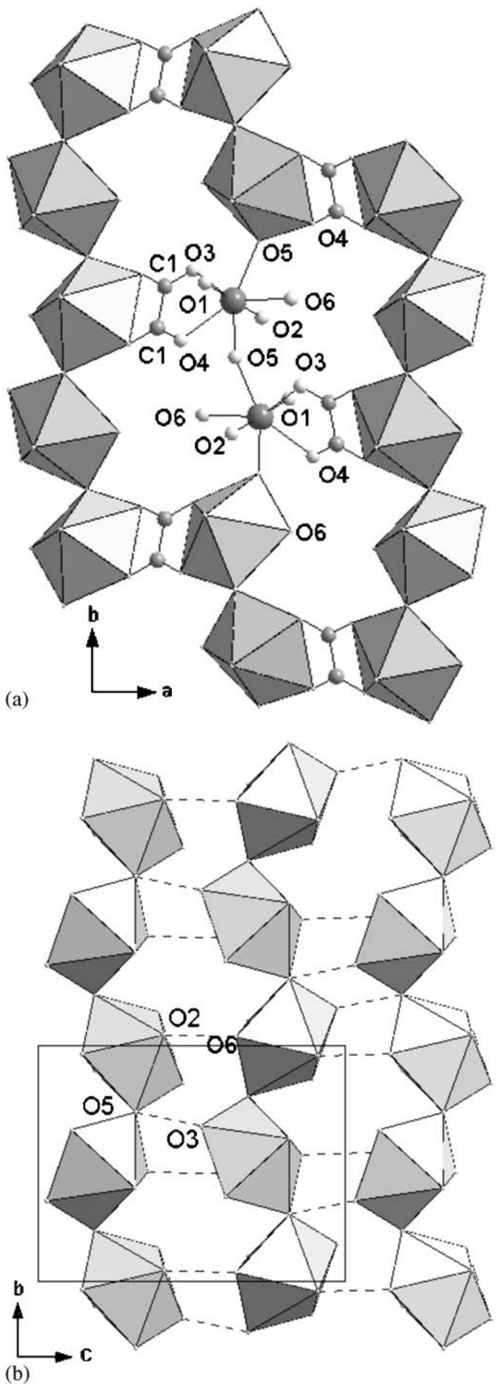

Fig. 3. Projection of the structure of **2** (a) on the (011) plane showing the two-dimensional arrangement of the linear chain SPBU of corner-shared pentagonal bipyramids linked by oxalate ions and (b) on the (100) plane showing the connection of the sheet by hydrogen bonds between parallel SPBU.

$[U_4O_{24}]$. Bridging oxalate ligands connect one tetrameric component further to four others to form puckered layers parallel to $(\bar{2}01)$ plane. Two types of cycles centered on inversion centers are formed, a four-membered ring $(U–OH)_4$ creating an unoccupied diamond-shaped site and a larger eight-membered ring $(U–OH–U–Ox)_4$ in which uranium atoms are alternatively connected by OH and oxalate groups. These large sites are occupied by the non-coordinating water molecules that are strongly linked by hydrogen bonds to the uranyl oxalate network involving the shortest $O\cdots O$ distances of 2.670(9) Å $(O(26)\cdots O(7))$ and 2.798(9) Å $(O(7)\cdots O(14))$. The cohesion between the layers is assured by hydrogen bonds where O(5) and O(5′) hydroxyl oxygen atoms are donor to uranyl oxygen O(12) and O(22) with $O\cdots O$ distances of 2.791(8) and 2.810(8), respectively (Fig. 4).

For the three compounds the valence bond sums of the oxygen atoms calculated without O–H bonds are in

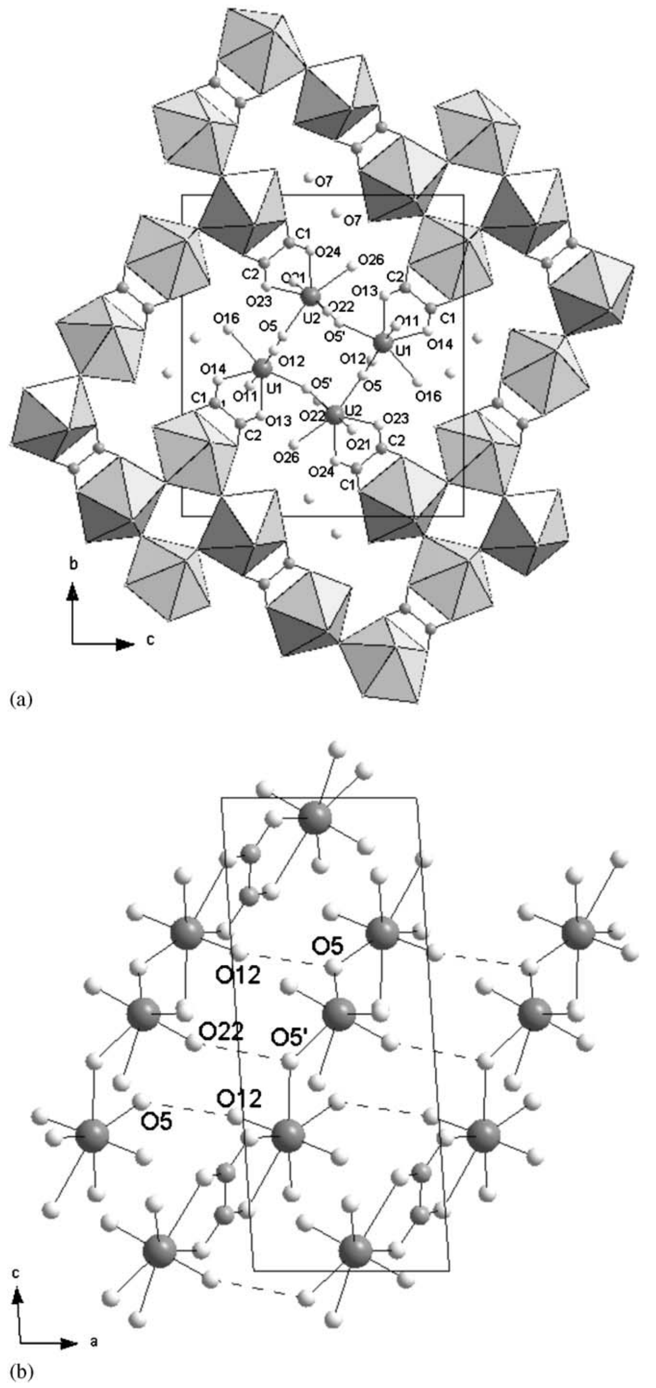

Fig. 4. Projection of the structure of **3** (a) on the (100) plane showing the two-dimensional arrangement of the tetrameric SPBU of corner-shared pentagonal bipyramids linked by oxalate ions and (b) on the (010) plane showing the connection of the layers by hydrogen bonds through the hydroxyl ions.

agreement with the identification of OH and $H_2O$ in the U(VI) polyhedra. The valence bond parameter for C–O were calculated with the parameters of Brese and O'Keeffe [46] (Table 7).

It is also interesting to describe the three structures from the same mixed structural building units of two $UO_7$ pentagonal bipyramids connected through an oxalate moiety. These planar units are further linked by hydroxyl oxygen atoms. The intra-dimer U–U distance is comparable to those observed in other compounds containing such dimers that are further connected through other oxalate ions (Table 8).

It is noteworthy that compounds **1**, **2** and **3** are the first representatives of the uranyl oxalatohydroxides. Two hydroxooxalato uranates have been reported, $Na_4[(UO_2)_2(C_2O_4)_2(OH)_4]$ [38,39] with an unknown structure and $NH_4[(UO_2)_2(C_2O_4)_2(OH)] \cdot 8H_2O$ [37]. In this last compound the structure is built from an other SPBU formed by two OH corner-shared $UO_7$ pentagonal bipyramids which contain in the equatorial base four oxygen from two oxalate entities that connect the SPBU in a 2D network. Recently the first neptunyl(V) oxalatohydroxide $Na_2[(NpO_2)(C_2O_4)(OH)] \cdot H_2O$ [47] has been reported; its structure is built from the same SPBU than **1**, but the equatorial base does not contain water oxygen; in fact the SPBU are connected through oxalate ions that are bidentate for one SPBU and monodentate for another making up a 1D chain.

## 5. Conclusion

By hydrothermal synthesis, we have prepared three compounds with structures containing 1D chains (**1**) or 2D

Table 7
Valence-bond sums for the oxygen atoms of uranyl ions (O(1)Ur and O(2)Ur), oxalate entity (O(3)Ox and O(4)Ox), hydroxyl ion (O(5)OH) and water molecule (O(6)$H_2O$) in the three compounds

| | Compound **1** | Compound **2** | Compound **3** | |
|---|---|---|---|---|
| | | | U(1) | U(2) |
| O(1)Ur | 1.74 | 1.74 | 1.73 | 1.72 |
| O(2)Ur | 1.73 | 1.75 | 1.70 | 1.70 |
| O(3)Ox | 1.92 | 1.90 | 1.89 | 1.87 |
| O(4)Ox | 1.98 | 1.86 | 1.89 | 1.93 |
| O(5)OH | 1.05 | 1.16 | 1.23 | 1.21 |
| O(6)$H_2O$ | 0.52 | 0.41 | 0.43 | 0.43 |

Table 8
U–U distances in uranyl-containing oxalates within the mixed structural building units formed by two $UO_7$ pentagonal bipyramids connected through an oxalate entity

| Compound | U–U distance | Ref |
|---|---|---|
| α-$[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ | 6.3304(17) | This study |
| β-$[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2]$ | 6.4248(14) | This study |
| $[(UO_2)_2(C_2O_4)(OH)_2(H_2O)_2] \cdot H_2O$ | 6.4066(9) | This study |
| $[(UO_2)(C_2O_4)(H_2O)] \cdot 2H_2O$ | 6.293(9)–6.313(8) | [32] |
| $NH_4[(UO_2)_2(C_2O_4)_2(OH)] \cdot 2H_2O$ | 6.076(72)–6.107(59) | [37] |
| $(NH_4)_2[(UO_2)_2(C_2O_4)_3]$ | 6.365(23) | [30] |
| $K_2[(UO_2)_2(C_2O_4)_3] \cdot 4H_2O$ | 6.190(5)–6.552(5) | [31] |
| $(NH_4)_2[(UO_2)_2(C_2O_4)_3] \cdot 3H_2O$ | 6.473(2)–6.483(9) | [23] |
| $(NH_4)(N_2H_5)[(UO_2)_2(C_2O_4)_3] \cdot 3H_2O$ | 6.515(17)–6.442(2) for U1<br>6.510(17)–6.452(2) for U2 | [23] |

networks (**2** and **3**) with the same composition $[UO_2]_2(C_2O_4)(OH)_2(H_2O)_2]$ built from $UO_7$ pentagonal bipyramids connected through OH groups to form SPBU further linked by $C_2O_4$ entities which act as bis-bidentates. In **2** the two OH groups of a $UO_7$ pentagonal bipyramid are in *trans* positions and permit the formation of chains. In **1** and **3**, the two OH groups are in *cis* positions. In **1** the SPBU is a dimeric cluster of edge-shared pentagonal bipyramids. In **3** the SPBU is a tetrameric unit of corner-shared pentagonal bipyramids. As for many other systems, hydrothermal synthesis is a magnificent tool to obtain numerous new and original architectures in the field of uranium chemistry.

*Auxiliary Material*: Further details of the crystal structures investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247 808 666; Email: crystaldata@fiz-karlsruhe.de) on quoting depository numbers CSD 415698, 415699, 415700.

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